Scattering functions for multicomponent mixtures of charged hard spheres, including the polydisperse limit. Analytic expressions in the Mean Spherical Approximation.

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Abstract

We present a closed analytical formula for the scattering intensity from charged hard sphere fluids with any arbitrary number of components. Our result is an extension to ionic systems of Vrij's analogous expression for uncharged hard sphere mixtures. Use is made of Baxter's factor correlation functions within the Mean Spherical Approximation (MSA). The polydisperse case of an infinite number of species with a continuous distribution of hard sphere diameters and charges is also considered. As an important by-product of our investigation, we present some properties of a particular kind of matrices (sum of the identity matrix with a *dyadic* matrix) appearing in the solution of the MSA integral equations for both uncharged and charged hard sphere mixtures. This analysis provides a general framework to deal with a wide class of MSA solutions having dyadic structure and allows an easy extension of our formula for the scattering intensity to different potential models. Finally, the relevance of our results for the interpretation of small angle neutron scattering experimental data is briefly discussed.

I. INTRODUCTION

Most of the naturally occurring or industrially important fluids are actually mixtures of more than two components. In particular, liquid mixtures of macroparticles (e.g., micellar or colloidal suspensions) exhibit size, shape and possibly charge distributions of their components. Macroparticles, unlike atoms, are intrinsecally polydisperse.

As a consequence, any rigorous statistical mechanical model of real mixtures should be able to include a large finite number p of species, which eventually will become infinite in the presence of polydispersity. In the latter case the properties of the mixtures will depend upon idealized continuous distributions of size, charge, etc..

Unfortunately, the presence of a large number of components poses challenging problems to the two major tools of the liquid state theory, namely computer simulation and integral equation (IE) methods. In fact, in the first case a prohibitively large number of particles may be required for a satisfactory Monte Carlo or molecular dynamics simulation, with consequently long and expensive computational times. In the second case, when the IEs must be solved numerically (as almost always occurs), the algorithms work with arrays formed by about $10^3 \times p^2$ elements, so that larger and larger amounts of memory and again of computational time are required as p increases; moreover, non-convergence problems in the numerical solution are encountered more frequently, especially in the presence of strong correlations and high density. Finally, polydisperse systems with infinitely-many components cannot be investigated in a fully adequate way if the IEs have to be solved numerically. In such cases, a discretization is unavoidable and one is forced to replace the continuous distribution of species with an appropriate p-component mixture, as shown by D'Aguanno et al. [1], [2], [3], [4], [5] who solved integral equations with $p \leq 10$ for Yukawa ($\equiv$ screened Coulomb) plus hard core interaction potentials. However, apart from the aforesaid work, most of the published IE studies on fluid mixtures concern binary or, more rarely, ternary systems [6], [7], [8].

In this paper we are interested in the static structural properties of multicomponent fluids. Experimentally, these can be efficiently monitored using X-ray, neutron and light scattering. Fitting experimental structure factors or scattering intensity of systems with a large number of components using IE theories is actually feasible only if the relevant equations do admit analytical solutions. Such a fortunate opportunity occurs only for peculiar interaction potentials and, to the best of our knowledge, this is limited to a single class of approximate equations.

The simplest case refers to the model mixture with hard sphere (HS) interactions. Using Baxter's analytical solution of the approximate Percus-Yevick (PY) integral equation for HS mixtures [9], Vrij [10] derived a closed expression for the scattering intensity $R(k)$ which holds true for *any* number p of components. It is remarkable that Vrij's formula depends on p only through the averages of some quantities. Hence, only the number of terms involved in these averages increases as p increases.This feature allows to extend the application of this equation for $R(k)$ to polydisperse HS mixtures [11]. The results are in a satisfactory agreement with Monte Carlo simulation data [12].

Independently and along a somewhat different route, Blum and Stell [13] presented the PY scattering function for polydisperse fluids of hard or permeable spheres in terms of Fourier transforms $H_{ij}(k)$ of the total correlation functions (some misprints are corrected in

Appendix A of of ref. [14]). In addition, the averages involved in Blum and Stell's expressions were evaluated analytically by Griffith et al. [15] in the case of polydisperse mixtures with a continuous Schultz distribution of diameters.

Now, apart from the HS case, we are unaware of a similar analytic determination of scattering functions for any other interaction potentials [16], [17]. The main purpose of the present paper is then to extend Vrij's work to multicomponent mixtures of charged particles.

The simplest model for charged systems is the so-called *primitive model,* consisting of an electroneutral mixture of charged hard spheres embedded in a dielectric continuum and interacting through unscreened Coulomb potentials. For these pair potentials, the unrestricted general solution, within the *Mean Spherical Approximation (MSA),* is available [18], [19], [20], [21]: simple analytical expressions for the Baxter factor correlation functions $q_{ij}(r)$ [9] are given and only a single non-linear equation in one parameter, Γ, has to be solved.

It is well known that, for dilute solutions of highly charged particles, the MSA may lead to unphysical negative values for some of the radial distribution functions $g_{ij}(r)$ close to the contact distance or in a neighborhood of the first minimum (in fact, the MSA is asymptotically correct for $r \to \infty$, but it is incorrect at short distances, in the region just outside the core). To overcome this drawback and extend the validity of the MSA to arbitrary low densities, some authors have proposed an *ad hoc* rescaling method, which replaces large electrostatic repulsions by appropriate HS repulsions [22], [23], [24] . Such a "rescaled mean spherical approximation" (RMSA) preserves the analytical form of the MSA solution and therefore allows an iterative fit of low density experimental data.

Nevertheless, in the regime of weakly charged solutions at sufficiently high concentrations, the MSA is expected to be a reasonably accurate approximation (in fact, the Coulomb part of the potentials can be considered as a perturbation with respect to the HS one, whereas in the above-mentioned opposite regime the electrostatic effects predominate over the HS repulsions).

The primitive model can be utilized for a large class of ionic fluid mixtures (electrolyte solutions, molten salts, solutions of macromolecules and polymers, micellar and colloidal suspensions, microemulsions, etc.) and with a careful analysis of the regime of validity for each case the MSA can be safely employed. For instance, Abramo et al. [25] applied the MSA analytic solution for charged HS to the evaluation of partial structure factors and x-ray diffraction patterns for the whole family of molten alkali halides (binary systems). Caccamo and Malescio [26] compared MSA and HNC (hypernetted-chain) results for structural and thermodynamic properties of polyelectrolytes (in particular, micellar solutions with an added electrolyte). We also note that Senatore and Blum [27] already performed MSA calculations of the average structure factor $S^M(k)$ for mixtures of charged HS with either size polydispersity or charge polydispersity. However, none of these authors presented closed-form analytical expressions for the MSA structure functions as in Vrij's work [10]; this is the task we have accomplished here.

The paper is organized as follows. In the next Section we briefly review the basic formalism of scattering and integral equation theory for multicomponent fluids. In Section III we discuss some useful properties of a peculiar class of matrices (related to dyadic matrices) encountered in the MSA solution for both neutral and charged HS mixtures (for uncharged HS the MSA coincides with the PY approximation). Section IV then provides the analytical MSA equations required to derive the new formula for the scattering intensity (and for the

average structure factor). This is described later on in Section V. The polydisperse limit is briefly discussed (Section VI) and, finally, in Section VII we summarize our results and comment on perspectives for future investigation.

II. SCATTERING AND INTEGRAL EQUATION THEORY

A. Scattering functions

The *coherent scattering intensity* $I(k)$ for a p-component fluid mixture with spherically symmetric interparticle interactions can be written in terms of the partial structure factors $S_{ij}(k)$ as [28]

$$R(k) \equiv I(k)/V = \sum_{i,j=1}^{p} (\rho_i \rho_j)^{1/2} F_i(k) F_j(k) S_{ij}(k) = \mathbf{f}^T(k) \mathbf{S}(k) \mathbf{f}(k) \tag{1}$$

Here, k is the magnitude of the scattering vector, V is the volume of the system, ρ_i the number density of species i. Further, $F_i(k) = F_i^0 B_i(k)$ denotes the scattering amplitude (or form factor) of species i, with F_i^0 being the scattering amplitude at zero angle and $B_i(k)$ the (angular averaged) intraparticle interference factor. The components of the column vector $\mathbf{f}(k)$ and of its transpose, the row vector $\mathbf{f}^T(k)$, are the form factors $F_i(k)$ weighted by means of the corresponding densities. More precisely, we define

$$f_i(k) = \rho_i^{1/2} F_i(k) \tag{2}$$

In order to get more compact formulas, often our notation slightly departs from Vrij's one [10]. Specifically, here this author uses f_i to denote our F_i^0.

Finally, $\mathbf{S}(k)$ is a symmetric matrix whose elements are the Ashcroft-Langreth partial structure factors $S_{ij}(k)$, defined by

$$S_{ij}(k) = \delta_{ij} + H_{ij}(k) = \delta_{ij} + (\rho_i \rho_j)^{1/2} \widetilde{h}_{ij}(k), \tag{3}$$

or, more concisely,

$$\mathbf{S}(k) = \mathbf{I} + \mathbf{H}(k), \tag{4}$$

with $\mathbf{I}$ being the unit matrix of order p (δ_{ij} = Kronecker delta). Here, $\widetilde{h}_{ij}(k)$ is the three-dimensional Fourier transform of the total correlation function, $h_{ij}(r) \equiv g_{ij}(r) - 1$, and $g_{ij}(r)$ is the radial distribution function between two particles of species i and j at a distance r.

In the short-wavelength limit $(k \to \infty)$, when the particles scatter the incident radiation independently, one has $\mathbf{S}(k \to \infty) = \mathbf{I}$ and therefore

$$R(k \to \infty) = \sum_{i=1}^{p} \rho_i F_i^2(k) = \mathbf{f}^T(k) \mathbf{f}(k) = |\mathbf{f}(k)|^2 \tag{5}$$

4

where $|\mathbf{f}(k)|$ denotes the magnitude of $\mathbf{f}(k)$. The normalized scattering intensity is also called the *effective structure factor* or the *measured average structure factor*

$$S^M(k) \equiv \frac{I(k)}{I(k \to \infty)} = \frac{\mathbf{f}^T(k)\,\mathbf{S}(k)\,\mathbf{f}(k)}{|\mathbf{f}(k)|^2} = 1 + \frac{\mathbf{f}^T(k)\,\mathbf{H}(k)\,\mathbf{f}(k)}{|\mathbf{f}(k)|^2} \tag{6}$$

B. Direct correlation functions

A second possible representation of the scattering functions can be obtained in terms of the three-dimensional Fourier transforms $\widetilde{c}_{ij}(k)$ of the direct correlation functions $c_{ij}(r)$. These functions are defined by the Ornstein-Zernike (OZ) integral equations of the liquid state theory, which, for systems with spherically symmetric interactions, read as

$$h_{ij}(r) = c_{ij}(r) + \sum_{m=1}^{p} \rho_m \int d\mathbf{r}'\; c_{im}(r')\, h_{mj}(|\mathbf{r} - \mathbf{r}'|) \tag{7}$$

Note that these equations can be solved only if they are coupled with a second relationship between $c_{ij}(r)$ and $h_{ij}(r)$. Such a "closure" consists of the exact formula

$$h_{ij}(r) = \exp\left[-\beta\phi_{ij}(r) + \gamma_{ij}(r) + B_{ij}(r)\right] - 1, \tag{8}$$

plus an approximation to the "bridge" function $B_{ij}(r)$, which is a complicated functional of $h_{ij}(r)$ and higher order correlation functions [29] ($\phi_{ij}(r)$ is the interparticle potential, $\beta \equiv 1/(k_B T)$, k_B is Boltzmann constant and T the absolute temperature; $\gamma_{ij}(r) \equiv h_{ij}(r) - c_{ij}(r)$).

By Fourier transforming the OZ convolution equations, these can be written in k-space as

$$[\mathbf{I} + \mathbf{H}(k)][\mathbf{I} - \mathbf{C}(k)] = \mathbf{I}, \tag{9}$$

with $C_{ij}(k) \equiv (\rho_i \rho_j)^{1/2}\, \widetilde{c}_{ij}(k)$. Since $\mathbf{S}(k) = \mathbf{I} + \mathbf{H}(k)$, we also get

$$\mathbf{S}(k) = [\mathbf{I} - \mathbf{C}(k)]^{-1}, \tag{10}$$

or, equivalently,

$$S_{ij}(k) = \frac{|\mathbf{I} - \mathbf{C}(k)|^{ji}}{|\mathbf{I} - \mathbf{C}(k)|}, \tag{11}$$

where $|\mathbf{I} - \mathbf{C}(k)|$ is the $p \times p$ determinant of the matrix $\mathbf{I} - \mathbf{C}(k)$ and $|\mathbf{I} - \mathbf{C}(k)|^{ji}$ is the cofactor of its (j, i)th element.

By substituting eq. (10) into eq. (1), we then obtain the scattering intensity in terms of the $\widetilde{c}_{ij}(k)$, i.e.,

$$R(k) = \mathbf{f}^T(k)\,[\mathbf{I} - \mathbf{C}(k)]^{-1}\,\mathbf{f}(k), \tag{12}$$

5

while the average structure factor is always given by $S^M(k) = R(k)/ |\mathbf{f}(k)|^2$.

For theoretical investigations all these formulas may be more useful than those in terms of the $\widetilde{h}_{ij}(k)$. In fact, in the cases in which the OZ equations have been analytically solved (for some particular interparticle potentials and with appropriate "closures") the $c_{ij}(r)$ have, in general, rather simple expressions, whereas the $h_{ij}(r)$ do not admit a simple analytic representation and are usually evaluated by numerical inverse Fourier transform of $\widetilde{h}_{ij}(k)$ (in k-space, the $\widetilde{h}_{ij}(k)$ are again much more involved than the $\widetilde{c}_{ij}(k)$).

C. Baxter factor correlation functions

Vrij [10] proposed a third representation of the scattering functions, in terms of the so-called Baxter factor correlation functions $q_{ij}(r)$. Baxter [9] showed, for hard sphere fluids, that the OZ equations can be transformed in an equivalent, but often easier to solve, form, by introducing a Wiener-Hopf factorization of the matrix $\mathbf{I} - \mathbf{C}(k)$. Later on Hiroike [32] extended Baxter's work to disordered fluids with any kind of spherically symmetric potentials and obtained generalized Baxter equations without using the Wiener-Hopf factorization.

Noting that $\mathbf{I} - \mathbf{C}(k)$ is a symmetric matrix and an even function of k, Baxter [9] suggested the following factorization

$$\mathbf{I} - \mathbf{C}(k) = \widehat{\mathbf{Q}}^T(-k)\,\widehat{\mathbf{Q}}(k) \tag{13}$$

where the elements of $\widehat{\mathbf{Q}}(k)$ are of the form

$$\widehat{\mathbf{Q}}(k) = \mathbf{I} - \widetilde{\mathbf{Q}}(k), \qquad \text{with} \qquad \widetilde{\mathbf{Q}}(k) = \int_{-\infty}^{+\infty} dr\ e^{ikr}\mathbf{Q}(r) \tag{14}$$

and

$$Q_{ij}(r) = 2\pi\,(\rho_i\rho_j)^{1/2}\,q_{ij}(r) \tag{15}$$

($\widehat{\mathbf{Q}}^T$ is the transpose of $\widehat{\mathbf{Q}}$). In general, in the analytically solvable cases, the factor correlation functions $q_{ij}(r)$ and $\widehat{Q}_{ij}(k)$ have a even simpler mathematical form than $c_{ij}(r)$ and $C_{ij}(k)$, respectively.

Substituting eq. (13) into eq. (10) yields

$$\mathbf{S}(k) = \widehat{\mathbf{Q}}^{-1}(k)\left[\widehat{\mathbf{Q}}^{-1}(-k)\right]^T \tag{16}$$

and, since

$$\widehat{Q}_{ij}^{-1}(k) = \frac{\left|\widehat{\mathbf{Q}}(k)\right|^{ji}}{\left|\widehat{\mathbf{Q}}(k)\right|}, \tag{17}$$

then

$$S_{ij}(k) = \sum_m \widehat{Q}_{im}^{-1}(k)\,\widehat{Q}_{jm}^{-1}(-k) = \frac{1}{D(k)}\sum_m \left|\widehat{\mathbf{Q}}(k)\right|^{mi}\left|\widehat{\mathbf{Q}}(-k)\right|^{mj} \tag{18}$$

6

with

$$D(k) \equiv \left|\widehat{\mathbf{Q}}(k)\right| \left|\widehat{\mathbf{Q}}(-k)\right| = |\mathbf{I} - \mathbf{C}(k)| \tag{19}$$

For the scattering intensity, plugging eq. (16) into eq. (1) and assuming that $\mathbf{f}(\mathbf{k}) = \mathbf{f}(-\mathbf{k})$ yields the simple expression

$$R(k) = \mathbf{s^T}(\mathbf{k})\,\mathbf{s}(-\mathbf{k}) = \frac{1}{\mathbf{D(k)}}\mathbf{L^T}(\mathbf{k})\,\mathbf{L}(-\mathbf{k}), \tag{20}$$

where we have defined

$$\mathbf{s}(\mathbf{k}) \equiv \left[\widehat{\mathbf{Q}}^{-1}(\mathbf{k})\right]^{\mathbf{T}}\mathbf{f}(\mathbf{k}) \equiv \frac{\mathbf{L}(\mathbf{k})}{\left|\widehat{\mathbf{Q}}(\mathbf{k})\right|} \tag{21}$$

The hypothesis $\mathbf{f}(\mathbf{k}) = \mathbf{f}(-\mathbf{k})$, which is equivalent to $F_i(k) = F_i(-k)$, is really correct for the physical systems we are concerned with in this paper. In fact, for homogeneous spheres with radius $\sigma_i/2$, it results that

$$F_i(k) \propto V_i \Phi_1(k\sigma_i/2), \tag{22}$$

where $V_i = (\pi/6)\,\sigma_i^3$ is the volume of a particle of species i and $\Phi_1(x)$ is an even function which may be expressed in terms of the first-order spherical Bessel function $j_1(x)$ as

$$\Phi_1(x) \equiv 3j_1(x)/x = 3(\sin x - x\cos x)/x^3 \tag{23}$$

Eq.s (16) and (20) give the partial structure factors and the scattering intensity in terms of the Baxter functions $\widehat{Q}_{ij}(k)$.

III. THE ANALYTICALLY TRACTABLE CASE OF DYADIC MATRICES

In view of producing theoretical expressions for the scattering functions, we have presented three possible routes, based upon different correlation functions, i.e., $H_{ij}(k)$, $C_{ij}(k)$ and $\widehat{Q}_{ij}(k)$, respectively.

In Baxter's route, followed in this paper, the crucial point for the analytic evaluation of the scattering functions is the possibility of getting a simple and closed expression for the inverse $\widehat{\mathbf{Q}}^{-1}(k)$ of the matrix $\widehat{\mathbf{Q}}(k)$. We want to emphasize that such a task can easily be accomplished if $\widehat{Q}_{ij}(k)$ has a particularly convenient structure of the following general form

$$\widehat{Q}_{ij}(k) = \delta_{ij} + \sum_{\mu=1}^{n} a_i^{(\mu)} b_j^{(\mu)} \equiv \delta_{ij} + \widehat{W}_{ij}(k) \tag{24}$$

Clearly, $\widehat{W}_{ij}(k)$ is simply related to the unidimensional Fourier transform $\widetilde{q}_{ij}(k)$ of $q_{ij}(r)$, i.e., $\widehat{W}_{ij}(k) = -2\pi\,(\rho_i\rho_j)^{1/2}\,\widetilde{q}_{ij}(k)$.

It is now convenient to recall that a second-rank tensor $T_{ij} = a_i b_j$ formed by the outer product of two vectors is sometimes represented by a symbol called a *dyad*, **ab**, and a linear

combination of dyads $\sum_{\mu} \lambda_{\mu} \mathbf{a}^{(\mu)} \mathbf{b}^{(\mu)}$ is called a *dyadic* [33]. In addition, as we propose here, a dyadic formed by a sum of n dyads might be called an *n-dyadic.*

Using this terminology, we could say that eq. (24) is equivalent to require that $\widetilde{q}_{ij}(k)$ is a generic *n*-dyadic matrix (of order p).

In the case of the PY solution for neutral HS mixtures (including the polydisperse limit), $\widetilde{q}_{ij}(k)$ is a 2-dyadic matrix [10], [13]. In the MSA solution for charged HS [19], as we shall better see in Section V, $\widetilde{q}_{ij}(k)$ becomes a 3-dyadic.

Both Vrij [10] and Blum with coworkers [13], [19] investigated some properties of these matrices, independently and from complementary points of view. On the one hand, Vrij emphasized the role of the rank of $\widehat{\mathbf{Q}}(k)$ and developed an original method to derive $\widehat{\mathbf{Q}}^{-1}(k)$. On the other hand, Blum and coworkers gave more directly closed expressions for $\widehat{\mathbf{Q}}^{-1}(k)$ for both 2- and 3-dyadics (on passing, we note that none of these authors uses our terminology; for instance, Blum and Høye [19] refer to these matrices as Jacobi matrices, whose inverse can be found for any size of the matrix).

In order to join and generalize the two above-mentioned approaches, in this Section we shall present some *general* properties of *n*-dyadic matrices, which hold true for any n (the relevant proofs are outlined in Appendix A).

Let us start from the fact that for any matrix of the form

$$M_{ij} = \delta_{ij} + \widehat{W}_{ij}, \tag{25}$$

where $\widehat{W}_{ij}$ is a generic $p \times p$ matrix (i.e., not necessarily a dyadic), the determinant $|\mathbf{M}|$ can be expressed by the following expansion in terms of principal minors

$$|\mathbf{M}| = \left| \mathbf{I} + \widehat{\mathbf{W}} \right| = 1 + \sum_{i=1}^{p} \widehat{W}_{ii} + \frac{1}{2!} \sum_{i,j=1}^{p} \begin{vmatrix} \widehat{W}_{ii} & \widehat{W}_{ij} \\ \widehat{W}_{ji} & \widehat{W}_{jj} \end{vmatrix}$$

$$+ \frac{1}{3!} \sum_{i,j,k=1}^{p} \begin{vmatrix} \widehat{W}_{ii} & \widehat{W}_{ij} & \widehat{W}_{ik} \\ \widehat{W}_{ji} & \widehat{W}_{jj} & \widehat{W}_{jk} \\ \widehat{W}_{ki} & \widehat{W}_{kj} & \widehat{W}_{kk} \end{vmatrix} + \cdots \tag{26}$$

For a generic $\widehat{W}_{ij}$ matrix, this expansion clearly stops at the p-th term. However, it is easy to show that, if $\widehat{W}_{ij}$ is an *n*-dyadic (with $n < p$), then any its minor having order $m > n$ vanishes! Using this along with some manipulations, we find our first basic result on dyadic matrices: *any $p \times p$ matrix of the form*

$$\mathbf{M} = \mathbf{I} + \sum_{\mu=1}^{n} \mathbf{a}^{(\mu)} \mathbf{b}^{(\mu)} \tag{27}$$

always has rank n, irrespective of p. Consequently, the expansion (26) of its determinant breaks off after the nth term and $|\mathbf{M}|$, which is of order p, turns out to be equal to a determinant D_M of order $n < p$, as expressed synthetically by

$$|\mathbf{M}| = D_M \equiv \det \left(\delta_{\mu\nu} + \mathbf{a}^{(\mu)} \cdot \mathbf{b}^{(\nu)} \right)_n \tag{28}$$

where $\det (...)_n$ means the determinant of a matrix of order n, while the dot denotes the usual scalar product of vectors

8

$$\mathbf{a}^{(\mu)} \cdot \mathbf{b}^{(\nu)} = \sum_{\mathbf{m}=\mathbf{1}}^{\mathbf{p}} \mathbf{a}_{\mathbf{m}}^{(\mu)} \mathbf{b}_{\mathbf{m}}^{(\nu)} \tag{29}$$

It is to be noted that the use of expansion (26) with 2-dyadics is originally due to Vrij [10]; the extension to $n > 2$ and eq. (28) are new.

Let us now consider the cofactors $|\mathbf{M}|^{ji}$ which will be needed in the calculation of the inverse matrix $\widehat{\mathbf{Q}}^{-1}(k)$ and, consequently, of the scattering intensity, as we shall discuss in Section V. In the same Appendix A it is also shown that for a matrix of the type (25) with a *generic* $\widehat{W}_{ij}$ the cofactors can be written as follows

$$|\mathbf{M}|^{ji} = |\mathbf{M}| \, \delta_{ij} - \widehat{U}_{ij} \tag{30}$$

where the following expansion for $\widehat{U}_{ij}$ holds true

$$\widehat{U}_{ij} = \widehat{W}_{ij} + \sum_{k=1}^{p} \begin{vmatrix} \widehat{W}_{ij} & \widehat{W}_{ik} \\ \widehat{W}_{kj} & \widehat{W}_{kk} \end{vmatrix} + \frac{1}{2!} \sum_{k,l=1}^{p} \begin{vmatrix} \widehat{W}_{ij} & \widehat{W}_{ik} & \widehat{W}_{il} \\ \widehat{W}_{kj} & \widehat{W}_{kk} & \widehat{W}_{kl} \\ \widehat{W}_{lj} & \widehat{W}_{lk} & \widehat{W}_{ll} \end{vmatrix} + \cdots \tag{31}$$

Again for n-dyadic matrices this expansion breaks off at the level $n < p$, as it is straightforward to check. Along the same lines as before, we find that $\widehat{U}_{ij}$ can be written as follows

$$\widehat{U}_{ij} = \sum_{\mu=1}^{n} a_i^{(\mu)} \widehat{D}_j^{(\mu)}, \tag{32}$$

where the $\widehat{D}_j^{(\mu)}$ are $n \times n$ determinants which can be obtained from the determinant D_M upon replacing the μ-th *row* with a row formed by $b_j^{(1)}, ..., b_j^{(n)}$.

From $M_{ij}^{-1} = |\mathbf{M}|^{ji} / |\mathbf{M}|$, it is now immediate to get the inverse matrix $\mathbf{M}^{-1}$

$$M_{ij}^{-1} = \delta_{ij} - \sum_{\mu=1}^{n} a_i^{(\mu)} \frac{\widehat{D}_j^{(\mu)}}{D_M}, \tag{33}$$

with

$$\widehat{D}_j^{(\mu)} \equiv \det \left([1 - \delta_{\alpha\mu}] \left[\delta_{\alpha\beta} + \mathbf{a}^{(\alpha)} \cdot \mathbf{b}^{(\beta)} \right] + \delta_{\alpha\mu} \, b_j^{(\beta)} \right)_n \tag{34}$$

This general formula constitutes our second result on dyadic matrices, yielding a new simple and elegant recipe which holds true for any n value: *the inverse of any $p \times p$ matrix* $\mathbf{M} = \mathbf{I} + \sum_{\mu=1}^{n} \mathbf{a}^{(\mu)} \mathbf{b}^{(\mu)}$ *has elements given by eq. (33) as linear functions of simple determinants* $\widehat{D}_j^{(\mu)}$ *of order n. The determinant* $\widehat{D}_j^{(\mu)}$ *is obtained from* D_M, *defined in eq. (28), by using a Cramer-like rule, i.e., by replacing the μ-th row with a row formed by* $b_j^{(1)}, ..., b_j^{(n)}$ (of course, all rows can be interchanged with the corresponding columns, without altering the value of the determinant).

Due to the symmetric role played by the a's and the b's in eq. (28), it is clear that one could derive an alternative expression to (32) with the role of the the a's and the b's interchanged.

Note that our formulas for $|\mathbf{M}|^{ji}$ and M_{ij}^{-1} are fully new with respect to Vrij's work [10]. Eq. (33) agrees with the expressions of M_{ij}^{-1} given by Blum and coworkers [13], [19] for $n = 2$ and $n = 3$; at the same time, our generalization offers a systematic way to calculate $\mathbf{M}^{-1}$ for any n.

We shall be using all these results in Section V.

IV. CHARGED HARD SPHERES AND MSA SOLUTION

The *primitive model* for ionic fluids consists of a p-component electroneutral mixture of charged hard spheres embedded in a continuum of dielectric constant ε (which may represent a possible solvent). The species i has diameter σ_i, number density ρ_i and electric charge $z_i e$ (e is the elementary charge). The interparticle potential is the hard sphere Coulombic one, i.e.,

$$
\phi_{ij}(r) = \begin{cases} +\infty & \text{for} \quad r < \sigma_{ij} \equiv \frac{1}{2}(\sigma_i + \sigma_j) \\[2mm] e^2 z_i z_j / (\varepsilon r) & \text{for} \quad r > \sigma_{ij} \end{cases}
\tag{35}
$$

and the electroneutrality condition reads

$$
\sum_m \rho_m z_m = 0
\tag{36}
$$

In r-space the Baxter form of the OZ equations which can be derived from eq. (13) is [9], [32]

$$
\begin{cases} rc_{ij}(|r|) = -q'_{ij}(r) + 2\pi \sum_m \rho_m \int_{\lambda_{mi}}^\infty dt \, q_{mi}(t) \, q'_{mj}(r+t), & r > \lambda_{ij} \equiv \frac{1}{2}(\sigma_i - \sigma_j) \\[2mm] rh_{ij}(|r|) = -q'_{ij}(r) + 2\pi \sum_m \rho_m \int_{\lambda_{im}}^\infty dt \, q_{im}(t)(r-t) h_{mj}(|r-t|), & r > \lambda_{ij} \end{cases}
\tag{37}
$$

where the prime denotes differentiation with respect to r. Note that, if $\lambda_{ij} < 0$, then r may assume negative values as well, although the correlation functions $c_{ij}(r)$ and $h_{ij}(r)$ are determined, of course, only for positive distances.

The Mean Spherical Approximation, used to solve these equations, consists of adding to the exact hard core condition

$$
h_{ij}(r) = -1 \qquad \text{for} \quad r < \sigma_{ij},
\tag{38}
$$

the approximate relationship

$$
c_{ij}(r) = -\beta\phi_{ij}(r) \qquad \text{for} \quad r > \sigma_{ij},
\tag{39}
$$

which is asymptotically correct for $r \to \infty$. For uncharged HS potentials, the MSA coincides with the PY approximation: $c_{ij}(r) = \{\exp[-\beta\phi_{ij}(r)] - 1\}[1 + h_{ij}(r) - c_{ij}(r)]$. The MSA, eq. (39), may also be regarded as the following approximation to the bridge functions

$$
B_{ij}(r) = \ln[1 + \gamma_{ij}(r) - \beta\phi_{ij}(r)] - [\gamma_{ij}(r) - \beta\phi_{ij}(r)] \qquad \text{for} \quad r > \sigma_{ij}
\tag{40}
$$

The solution of the MSA integral equations for the most general case of ions with arbitrary charges and diameters was found by Blum [18], [19], [20], [21]. It is worth noting that Blum employed a form of the Baxter equations which is slightly different from eq.s (37). In this paper it proves convenient to follow the original form proposed by Baxter [9] and Hiroike [32], eq.s (37), and used by Vrij [10]. The differences from Blum's formulas of ref.

[19] are, however, small (a detailed comparison is given in Appendix B). Our modified form of the MSA solution reads

$$
q_{ij}(r) = \begin{cases} 0, & r < \lambda_{ij} \\[2mm] \frac{1}{2}(r - \sigma_{ij})^2 q_i{}'' + (r - \sigma_{ij}) q_{ij}' - A_i z_j, & \lambda_{ij} < r < \sigma_{ij} \\[2mm] -A_i z_j, & r > \sigma_{ij} \end{cases} \tag{41}
$$

The coefficients of the factor correlation functions are given by

$$
q_{ij}' = \frac{1}{\Delta}\left(\sigma_{ij} + \frac{3\xi_2}{2\Delta}\sigma_i\sigma_j\right) - \frac{\Gamma^2}{\ell_B}A_iA_j \tag{42}
$$

$$
q_i{}'' = \frac{1}{\Delta}\left(1 + \frac{3\xi_2}{\Delta}\sigma_i\right) + A_iP_z \tag{43}
$$

$$
A_i = \frac{\ell_B}{\Gamma}\,\frac{z_i - \frac{1}{2}\sigma_i^2 P_z}{1 + \Gamma\sigma_i} \tag{44}
$$

with

$$
\xi_n = \frac{\pi}{6}\sum_m \rho_m\sigma_m^n \qquad (n = 2, 3) \tag{45}
$$

$$
\Delta = 1 - \xi_3 \tag{46}
$$

$$
\ell_B = \beta e^2/\varepsilon \qquad \text{(Bjerrum length)} \tag{47}
$$

$$
P_z = \frac{1}{\Omega}\sum_m \frac{\rho_m\sigma_m z_m}{1 + \Gamma\sigma_m} \tag{48}
$$

$$
\Omega = 1 - \xi_3 + \frac{\pi}{2}\sum_m \frac{\rho_m\sigma_m^3}{1 + \Gamma\sigma_m} \tag{49}
$$

Finally, the value of the parameter Γ can be determined by solving numerically the following consistency equation

$$
(2\Gamma)^2 = 4\pi\ell_B\sum_m \rho_m\left(\frac{z_m - \frac{1}{2}\sigma_m^2 P_z}{1 + \Gamma\sigma_m}\right)^2, \tag{50}
$$

which is equivalent to the condition

$$
\sum_m \rho_m A_m^2 = \ell_B/\pi \tag{51}
$$

11

In the limit of point ions (all $\sigma_m \to 0$), 2Γ tends to the Debye inverse shielding length κ_D of the classical Debye-Hückel theory for electrolyte solutions, while for finite size ions $(2\Gamma)^{-1}$ is always larger than κ_D :

$$2\Gamma \leq \kappa_D \equiv \left(4\pi \ell_B \sum_m \rho_m z_m^2 \right)^{1/2} \tag{52}$$

There is a striking similarity of the MSA to the Debye-Hückel theory, with 2Γ taking the place of κ_D (2Γ is the correct screening parameter for finite size ions).

It is to be noted that the degree of the algebraic equation (50) for Γ increases with the number p of components in the mixture. Moreover, among all its solutions, only one is physically acceptable: the one which is positive and tendes to κ_D from below in the infinite dilution limit.

V. APPLICATION OF DYADIC PROPERTIES TO CHARGED HARD SPHERES

A. The inverse matrix $\widehat{\mathbf{Q}}^{-1}(k)$

The starting point is the evaluation of the unidimensional Fourier transform, $\widetilde{q}_{ij}(k)$, of the MSA solution for $q_{ij}(r)$. The resulting $\widehat{Q}_{ij}(k)$ can be written as

$$\widehat{Q}_{ij}(k) = \delta_{ij} + \widehat{W}_{ij}(k) = \delta_{ij} + (\rho_i \rho_j)^{1/2} W_{ij}(k), \tag{53}$$

with

$$W_{ij}(k) = -2\pi \widetilde{q}_{ij}(k) = e^{ik\sigma_i/2} \left[\alpha_j(k) + \sigma_i \beta_j(k) + A_i \gamma_j(k) \right]$$

$$= Z_{ij}(k) + e^{iX_i} A_i \gamma_j(k) \tag{54}$$

where i - when it is not a subscript - is the imaginary unit and

$$X_m = k\sigma_m/2 \tag{55}$$

$$\alpha_j(k) = \frac{4\pi}{\Delta} \frac{1}{k^3} (\sin X_j - X_j \cos X_j) = \frac{\pi}{6} \sigma_j^3 \frac{1}{\Delta} \Phi_1(X_j) \tag{56}$$

$$\beta_j(k) = \beta_{0,\,j}(k) + \beta_{1,\,j}(k) \tag{57}$$

$$\beta_{0,\,j}(k) = \frac{2\pi}{\Delta} \frac{\sigma_j}{k} \sin X_j \equiv \frac{\pi}{6} \sigma_j^2 \frac{1}{\Delta} \Phi_0(X_j) \tag{58}$$

$$\beta_{1,\,j}(k) = \left(\frac{3\xi_2}{\Delta} - \frac{1}{2} ik \right) \alpha_j(k) \tag{59}$$

$$\gamma_j(k) = \gamma_{0,\,j}(k) + \gamma_{1,\,j}(k) + \gamma_{2,\,j}(k) \tag{60}$$

$$\gamma_{0,\,j}\left(k\right) \;=\; \frac{\Gamma^2 A_j}{\ell_B}\,\frac{4\pi i}{k^2}\,\sin X_j \tag{61}$$

$$\gamma_{1,\,j}\left(k\right) \;=\; \frac{\Gamma A_j}{\ell_B}\,\frac{2\pi i}{k}\,e^{-iX_j} \tag{62}$$

$$\gamma_{2,\,j}\left(k\right) \;=\; P_z\,\Delta\left[\alpha_j\left(k\right) + \frac{2i}{k}\beta_{0,\,j}\left(k\right)\right] \tag{63}$$

Here, the function $\Phi_1\left(x\right) = 3j_1(x)/x$ is the same as in eq. (23) and we can also write $\Phi_0\left(x\right)$ in terms of Bessel functions: $\Phi_0\left(x\right) = 3j_0(x) = 3\sin x/x$.

Note that $\alpha_j\left(k\right)$ and $\beta_{0,\,j}\left(k\right)$ are even functions, unlike $\beta_j\left(-k\right) = \beta_j^*\left(k\right)$ and $\gamma_j\left(-k\right) = \gamma_j^*\left(k\right)$ (the asterisk denotes complex conjugation). Hence, we have $W_{ij}\left(-k\right) = W_{ij}^*\left(k\right)$ and $\widehat{Q}_{ij}\left(-k\right) = \widehat{Q}_{ij}^*\left(k\right)$.

Moreover, $Z_{ij}\left(k\right)$ is the pure hard sphere term considered by Vrij, while $e^{iX_i}A_i\gamma_j\left(k\right)$ is the electrostatic contribution (α_j and β_j correspond to M_j and N_j of ref. [10], respectively).

In the limit {all charges z_m} $\to 0$, A_i, P_z and $\gamma_j(k)$ vanish simultaneously. In the long wavelength limit ($k \to 0$), $Z_{ij}(k)$ tends to a finite value, whereas $\gamma_j(k)$ diverges as k^{-1}. Such a singularity of $\widetilde{q}_{ij}\left(k\right)$ implies a k^{-2} divergence of $\widetilde{c}_{ij}\left(k\right)$; however, all this does not influence the structure factors, which remain finite at the origin.

The crucial point is now that, according to eq. (54), the MSA expression of $W_{ij}\left(k\right)$ for charged HS mixtures is a 3-dyadic. As we discussed in Sec. II, this peculiar form of $\widehat{Q}_{ij}\left(k\right)$ allows to write down a simple and compact expression for its $p \times p$ determinant $\left|\widehat{\mathbf{Q}}\left(k\right)\right| = \left|\mathbf{I} - \widetilde{\mathbf{Q}}\left(\mathbf{k}\right)\right|$. Using the result (28) we get immediately, for any p,

$$\begin{vmatrix} \widehat{Q}_{11}\left(k\right) & \cdots & \widehat{Q}_{1M}\left(k\right) \\ \vdots & \ddots & \vdots \\ \widehat{Q}_{M1}\left(k\right) & \cdots & \widehat{Q}_{MM}\left(k\right) \end{vmatrix} = D_Q(k) \equiv \begin{vmatrix} 1 + \langle\alpha\rangle & \langle\beta\rangle & \langle\gamma\rangle \\ \langle\sigma\alpha\rangle & 1 + \langle\sigma\beta\rangle & \langle\sigma\gamma\rangle \\ \langle A\alpha\rangle & \langle A\beta\rangle & 1 + \langle A\gamma\rangle \end{vmatrix}, \tag{64}$$

where we have defined

$$\langle fg\rangle \equiv \sum_m \rho_m e^{iX_m} f_m(k)g_m(k) \tag{65}$$

Notice that our shorthand notation is somewhat different from Vrij's one. Of course, $\langle\alpha\rangle$, $\langle\beta\rangle$, etc. are complex functions of k. However, as in eq. (64), we shall mostly omit the argument, unless when necessary. The connection with the a's and b's is

$$a_i^{(1)} = \rho_i^{1/2} e^{iX_i}, \qquad b_j^{(1)} = \rho_j^{1/2}\alpha_j$$

$$a_i^{(2)} = \rho_i^{1/2} e^{iX_i}\sigma_i, \qquad b_j^{(2)} = \rho_j^{1/2}\beta_j \tag{66}$$

$$a_i^{(3)} = \rho_i^{1/2} e^{iX_i}A_i, \qquad b_j^{(3)} = \rho_j^{1/2}\gamma_j$$

Eq. (64) clearly stresses the fact that, even if the order of the determinant $\left|\widehat{\mathbf{Q}}\left(k\right)\right|$ may become quite large with increasing the number p of components in the mixture, nevertheless $D_Q(k)$ remains of order 3 (*contraction or reduction effect*).

13

From $\left|\widehat{\mathbf{Q}}(k)\right| = D_Q(k)$ and eq. (19), it follows that

$$D(k) = |\mathbf{I} - \mathbf{C}(k)| = D_Q(k)D_Q(-k) = D_Q(k)D_Q^*(k) \tag{67}$$

Once again, $D(k) = |\mathbf{I} - \mathbf{C}(k)|$ is a determinant of order p, whereas $D_Q(k)D_Q(-k)$ is a product of two determinants of order three. Since $|\mathbf{A}||\mathbf{B}| = |\mathbf{AB}|$ (if $\mathbf{A}$ and $\mathbf{B}$ are any two square matrices of the same order), $D_Q(k)D_Q(-k)$ could be rewritten as a single determinant of order 3. We can thus conclude that, under the peculiar assumptions of our model, also the matrix $\mathbf{I} - \mathbf{C}(k)$ has always rank 3, no matter how large is the number p of components.

Similar considerations hold true for the cofactor matrices. From eq.s (30) and (32) one can easily show, after some manipulations, that

$$\left|\widehat{\mathbf{Q}}(k)\right|^{ji} = \left|\widehat{\mathbf{Q}}(k)\right|\delta_{ij} - (\rho_i\rho_j)^{1/2}\, e^{iX_i}\left[D_j^{(1)}(k) + \sigma_i D_j^{(2)}(k) + A_i D_j^{(3)}(k)\right], \qquad (i,j = 1, ..., p) \tag{68}$$

where $D_j^{(\mu)}$ ($\mu = 1, 2, 3$) is simply defined as the 3×3 determinant derived from D_Q by replacing its mth row with the vector $(\alpha_j,\ \beta_j,\ \gamma_j)$.

Then, from $\widehat{Q}_{ij}^{-1}(k) = \left|\widehat{\mathbf{Q}}(k)\right|^{ji} / \left|\widehat{\mathbf{Q}}(k)\right|$, it is now immediate to get the inverse matrix of $\widehat{\mathbf{Q}}(k)$

$$\widehat{\mathbf{Q}}^{-1}(k) = \mathbf{I} - \widehat{\mathbf{V}}(k) \tag{69}$$

with

$$\widehat{V}_{ij}(k) \equiv (\rho_i\rho_j)^{1/2}\, V_{ij}(k) \equiv (\rho_i\rho_j)^{1/2}\, e^{iX_i}\left[\alpha_j{}'(k) + \sigma_i\beta_j{}'(k) + A_i\gamma_j{}'(k)\right], \tag{70}$$

$$\alpha_j{}'(k) \equiv \frac{D_j^{(1)}(k)}{D_Q(k)}, \qquad \beta_j{}'(k) \equiv \frac{D_j^{(2)}(k)}{D_Q(k)}, \qquad \gamma_j{}'(k) \equiv \frac{D_j^{(3)}(k)}{D_Q(k)} \tag{71}$$

Here, the prime does not denote a derivative: we have used this notation only to emphasize the similarity of the form of $V_{ij}(k)$ to that of $W_{ij}(k)$ in $\widehat{Q}_{ij}(k)$.

B. Scattering intensity

To get the scattering intensity

$$R(k) = \sum_j s_j(k)\ s_j(-k), \tag{72}$$

where

$$s_j(k) = \frac{kL_j(k)}{kD_Q(k)}, \tag{73}$$

let us first evaluate

14

$$L_j(k) = \sum_m \rho_m^{1/2} F_m(k) \left|\widehat{\mathbf{Q}}(k)\right|^{jm} \tag{74}$$

Note that in eq. (73) both the numerator and the denominator have been multiplied by k to "heal" the k^{-1} singularity of $\gamma_j(k)$ at the origin and ensure that in numerical calculations $R(k)$ has a regular behaviour as $k \to 0$.

If the expression (68) for $\left|\widehat{\mathbf{Q}}(k)\right|^{jm}$ is inserted in this equation, then, after some manipulations, $L_j(k)$ can be cast in a very convenient form as a 4×4 determinant, i.e.,

$$L_j(k) = \rho_j^{1/2} \begin{vmatrix} F_j & \alpha_j & \beta_j & \gamma_j \\ \langle F \rangle & 1 + \langle \alpha \rangle & \langle \beta \rangle & \langle \gamma \rangle \\ \langle \sigma F \rangle & \langle \sigma \alpha \rangle & 1 + \langle \sigma \beta \rangle & \langle \sigma \gamma \rangle \\ \langle AF \rangle & \langle A\alpha \rangle & \langle A\beta \rangle & 1 + \langle A\gamma \rangle \end{vmatrix} \tag{75}$$

However, to perform the summation over j, it is more convenient to re-expand this determinant along the first row

$$L_j(k) = \rho_j^{1/2} \left[F_j(k) T_1(k) + \alpha_j(k) T_2(k) + \beta_j(k) T_3(k) + \gamma_j(k) T_4(k) \right], \tag{76}$$

where $T_\mu(k)$ $(\mu = 1, ..., 4)$ is the cofactor of the $(1, \mu)$th element of the first row. Clearly, $T_1(k) = D_Q(k)$.

In this way we obtain

$$R(k) = \begin{cases} \{F^2\} & + \{F\alpha\}\, C_1^* & + \{F\beta\}\, C_2^* & + \{F\gamma\}\, C_3^* \\[2mm] + \{\alpha F\}\, C_1 & + \{\alpha^2\}\, C_1 C_1^* & + \{\alpha\beta^*\}\, C_1 C_2^* & + \{\alpha\gamma^*\}\, C_1 C_3^* \\[2mm] + \{\beta F\}\, C_2 & + \{\beta\alpha\}\, C_2 C_1^* & + \{\beta\beta^*\}\, C_2 C_2^* & + \{\beta\gamma^*\}\, C_2 C_3^* \\[2mm] + \{\gamma F\}\, C_3 & + \{\gamma\alpha\}\, C_3 C_1^* & + \{\gamma\beta^*\}\, C_3 C_2^* & + \{\gamma\gamma^*\}\, C_3 C_3^* \end{cases} \tag{77}$$

with

$$\{fg\} \equiv \sum_m \rho_m f_m(k)\, g_m(k) \tag{78}$$

$$C_\mu(k) \equiv T_{\mu+1}(k)/T_1(k) \qquad (\mu = 1, 2, 3) \tag{79}$$

Clearly, $\{F^2\}$ is identical to $\mathbf{f}^{\mathbf{T}}\mathbf{f}$.

This simple and elegant expression for $R(k)$ arises in a quite general way from the dyadic structure of $\widetilde{q}_{ij}(k)$ (only some properties of α_j were added, i.e., $\alpha_j(-k) = \alpha_j(k) = \alpha_j^*(k)$). Of course, such a formula might be used as is. Nevertheless, from a practical point of view, it is more convenient to take advantage of the particular, explicit, expressions for α_j, β_j and γ_j in the present model, in order to achieve a sort of "reduction" of the above-written result. Since simpler expressions are preferable for numerical calculations, we have tried to perform all possible simplifications, starting from the determinant form of $L_j(k)$ and using some properties of determinants.

The first step is to take the determinant form of $L_j(k)$, eq. (75), and subtract from the third column the second one multiplied by $(3\xi_2/\Delta - ik/2)$. Since $\beta_{1,\,j}$ is given by eq. (59), such on operation "eliminates" $\beta_{1,\,j}$ from the third column, which becomes

$$\beta_{0,\,j}$$

$$\langle\beta_0\rangle - \frac{3\xi_2}{\Delta} + \frac{1}{2}ik$$

$$1 + \langle\sigma\beta_0\rangle \tag{80}$$

$$\langle A\beta_0\rangle$$

The advantage of the resulting expression for $L_j(k)$ is that, in place of the complex functions β_j, it involves only the $\beta_{0,\,j}$, which are real and even. It is worth noting that such a reduction is implicit in Vrij's work [10].

Let us now transform the electrostatic contributions. Our second step "eliminates" $\gamma_{2,\,j}$ from the fourth column. Looking at eq. (63), it is evident that it is now necessary to subract a linear combination of the second column and the third one (in the new form with $\beta_{0,\,j}$), multiplied respectively by $P_z\,\Delta$ and $2iP_z\,\Delta\,/k$. The fourth column becomes

$$\gamma_{01,\,j} \equiv \gamma_{0,\,j} + \gamma_{1,\,j}$$

$$\langle\gamma_{01}\rangle + \frac{2i}{k}3\xi_2 P_z$$

$$\langle\sigma\gamma_{01}\rangle - \frac{2i}{k}P_z\Delta \tag{81}$$

$$1 + \langle A\gamma_{01}\rangle$$

As a further step, we have observed that the particular functional form of $\gamma_{1,\,j}(k)$ allows a direct analytic evaluation of the necessary averages relevant to this term. By deriving from eq.s (44),(48), (49) and from the electroneutrality condition the following new identities

$$\{A\} \equiv \sum_m \rho_m A_m = -\frac{\ell_B}{\pi\Gamma}P_z\left(3\xi_2 + \Gamma\Delta\right) \tag{82}$$

$$\{\sigma A\} \equiv \sum_m \rho_m \sigma_m A_m = \frac{\ell_B}{\Gamma}P_z\Delta, \tag{83}$$

together with eq. (51) for $\{A^2\} \equiv \sum_m \rho_m A_m^2 = \ell_B/\pi$, we find

$$\langle\gamma_1\rangle = -i\frac{2}{k}P_z\left(3\xi_2 + \Gamma\Delta\right) \tag{84}$$

$$\langle\sigma\gamma_1\rangle = i\frac{2}{k}P_z\Delta \tag{85}$$

$$\langle A\gamma_1\rangle = i\frac{2\Gamma}{k} \tag{86}$$

16

Putting all these results together and multiplying $L_j(k)$ by k to "regularize" its behaviour at $k = 0$ (as proposed in eq. (73)) we get

$$kL_j(k) = \rho_j^{1/2} \begin{vmatrix} F_j & \alpha_j & \beta_{0,\,j} & k\gamma_{01,\,j} \\ \langle F \rangle & 1 + \langle \alpha \rangle & \langle \beta_0 \rangle - 3\xi_2/\Delta + ik/2 & k\langle \gamma_0 \rangle - 2\pi iP_z\Gamma\Delta \\ \langle \sigma F \rangle & \langle \sigma \alpha \rangle & 1 + \langle \sigma\beta_0 \rangle & k\langle \sigma\gamma_0 \rangle \\ \langle AF \rangle & \langle A\alpha \rangle & \langle A\beta_0 \rangle & k\left[1 + \langle A\gamma_0 \rangle\right] + i2\Gamma \end{vmatrix} \qquad (87)$$

where

$$\gamma_{01,\,j}(k) \equiv \gamma_{0,\,j}(k) + \gamma_{1,\,j}(k) = \frac{\Gamma A_j}{\ell_B}\frac{2\pi}{k}\left[\sin X_j + i\left(\cos X_j + \frac{2\Gamma}{k}\sin X_j\right)\right] \qquad (88)$$

This new form for $kL_j(k)$ is really more convenient than that corresponding to eq. (75), since it requires a smaller number of numerical calculations and allows to write a simpler expression for the scattering intensity. In fact, expanding the aforesaid determinant along the first line and taking into account that F_j, α_j and $\beta_{0,\,j}$ are real and even functions, we get after some algebra the following final result for $R(k)$

$$R(k) = R_1(k) + R_2(k), \qquad (89)$$

$$R_1(k) = \left\{F^2\right\} + \left\{\alpha^2\right\}C_1C_1^* + \left\{\beta_0^2\right\}C_2C_2^* \qquad (90)$$
$$+ 2\text{Re}\left[\left\{F\alpha\right\}C_1 + \left\{F\beta_0\right\}C_2 + \left\{\alpha\beta_0\right\}C_1C_2^*\right]$$

$$R_2(k) = k^2\left\{\gamma_{01}\gamma_{01}^*\right\}C_3C_3^* \qquad (91)$$
$$+ 2k\,\text{Re}\left[\left\{\gamma_{01}F\right\}C_3 + \left\{\gamma_{01}\alpha\right\}C_3C_1^* + \left\{\gamma_{01}\beta_0\right\}C_3C_2^*\right]$$

where $\text{Re}\left[...\right]$ denotes the real part of a complex value function and the C_μ used here are not the same as those in eq. (77): their definition is again given by eq. (79) but the cofactors $T_\mu(k)$ now refer to the new determinant expression for $kL_j(k)$, i.e., to eq. (87). Note that $T_1(k) = kD_Q(k)$.

Observe that $\left\{F\alpha\right\}$, $\left\{F\beta_0\right\}$ and $\left\{\alpha\beta_0\right\}$ are real quantities, while the $\gamma_{0,\,j}(k)$ are odd and purely imaginary functions, i.e., $\gamma_{0,\,j}(-k) = -\gamma_{0,\,j}(k) = \gamma_{0,\,j}^*(k)$.

In the limit of {all charges $z_m \to 0$}, it results that $R_2(k) \to 0$ and $R_1(k) \to R^{HS}(k)$, i.e., we recover exactly (apart from the notation) Vrij's formula for the neutral HS case.

Finally, as concerns the partial structure factors, they can easily be evaluated by means of eq.s (16) and (69)-(71), but we prefer not to give their explicit expressions here.

VI. THE POLYDISPERSE LIMIT

In the treatment of polydisperse systems it is customary to start from a mixture with a finite number of components and then to perform a limiting process, which results into a continuous distribution of the properties which characterize the species (*identity variables*) [34]. In other words, in an IE approach one first solves the equations and then takes the infinite-species limit. This is a delicate point.

Still in the IE framework, we like to emphasize a second alternative route, i.e., the possibility of taking the infinite-species limit from the outset. According to this second viewpoint; one first sets up integral equations for polydisperse fluids and then tries to solve them. It is worth mentioning that, although a polydisperse version of the OZ equations for HS has already appeared in the literature [14], we are unaware of any papers where polydisperse Baxter integral equations have been proposed.

To this aim, let us first recall how the composition of polydisperse systems can be specified. In a "fully polydisperse" mixture the discrete variable $1 \leq i \leq p$ that labels the species is replaced by a set of one, two or more continuous variables, which constitute an *identity vector* $\mathbf{I} = \{\mathbf{I_1}, \mathbf{I_2}, ..., \mathbf{I_s}\}$ (not to be confused with the previously used identity matrix). The identity variables are distributed according to a multivariable *molar fraction density function* $p(\mathbf{I})$ [34], [35], [36]: the molar fraction $x_i = \rho_i/\rho = \rho_i/\sum_m \rho_m$ of the discrete case goes into

$$p(\mathbf{I})\mathbf{dI} = \mathbf{p(I_1, I_2, ..., I_s)dI_1 dI_2...dI_s}, \tag{92}$$

which is the probability of finding a particle with species labels in the identity range $(\mathbf{I}, \mathbf{I+dI})$. As a consequence, for the number density it results that

$$\rho_i \rightarrow \rho p(\mathbf{I})d\mathbf{I}, \tag{93}$$

with ρ being the total number density.

In the opposite case of "fully monodisperse" mixtures, one could write

$$p(\mathbf{I}) = \sum_{\{\mathbf{I'}\}} \mathbf{x}(\mathbf{I'})\, \delta(\mathbf{I} - \mathbf{I'}), \tag{94}$$

where $\{\mathbf{I'}\}$ is the set of identity vectors corresponding to discrete species present in the finite amounts $\{x(\mathbf{I'})\}$ (here, δ is the Dirac delta distribution).

Of course, one may also consider "partly polydisperse" mixtures in which several species are monodisperse, while the remaining ones are polydisperse. In this case, the distribution function $p(\mathbf{I})$ is the sum of a discrete part, $p_d(\mathbf{I})$, like that in eq. (94) and a continuous one, $p_c(\mathbf{I})$. Clearly, to be a probability density function, $p(\mathbf{I})$ must satisfy the normalization condition

$$\sum_{\{\mathbf{I'}\}} x(\mathbf{I'}) + \int d\mathbf{I} \; \mathbf{p_c(I)} = \mathbf{1} \tag{95}$$

Bearing all this in mind, it is immediate to pass from the Baxter equations (37) for p-component mixtures to those for polydisperse fluids, using the following the replacement

$$\sum_m \rho_m \; ... \rightarrow \int d\rho_m \; ... = \rho \int d\mathbf{I} \; \mathbf{p(I)} \; ..., \tag{96}$$

if we re-interpret the species label m as a shorthand notation for the identity vector $\mathbf{I}$, whose distribution function $p(\mathbf{I})$ may include both a continuous and a discrete part, respectively for polydisperse and monodisperse components.

Using this simple convention, the procedure of solving the polydisperse Baxter equations for uncharged or charges HS, within the MSA, is formally the same as in the monodisperse

18

case, apart from the substitution required by eq. (96). In other words, we can conclude that, at least for the two aforesaid systems, the MSA solution for the polydisperse case can be obtained from the monodisperse one via the simple prescription expressed by eq. (96). Note that all this fully agrees with the findings by Stell and coworkers [13], [37] for neutral HS in the PY approximation and with the MSA investigation performed by Senatore and Blum [27] on mixtures of charged HS with either size polydispersity (and fixed charge value) or charge polydispersity (and fixed diameter).

Before concluding this Section, it is to be noted that, while for HS a single identity variable - the diameter - is sufficient to characterize a species (i.e., $\mathbf{I} = \{\sigma\}$), for charged HS two variables - the diameter and the charge - are necessary (i.e., $\mathbf{I} = \{\sigma, \mathbf{z}\}$). To avoid the difficulty of working with a two-variable distribution $p(\sigma, z)$, one might assume a strong correlation between σ and z, reducing the number of independent variables to only one. It is customary to express such a relationship in the form $z = z(\sigma)$ [27], [44], but perhaps the inverse function $\sigma = \sigma(z)$ might be preferred in view of the integrations to be done over the remaining independent variable (recall that the range of σ is $[0, +\infty[$, while z varies in the interval $]-\infty, +\infty[$). Anyway, for macroions of colloidal suspensions it is reasonable to assume that their charges scale linearly with their surface area, i.e., $z \propto \sigma^2$, keeping the surface charge density constant [1], [2], [5].

VII. CONCLUDING REMARKS

The first and main result of this paper is given by eq.s (89)-(91), which provide a new MSA formula for the scattering intensity from multicomponent mixtures of charged hard spheres. This fills an important gap present so far in the relevant literature. It can be applied to a wide variety of ionic fluids and is expected to be particularly useful to fit experimental data.

Our result extends Vrij's one for neutral HS and reduces to it in the limit of vanishing electrostatic contributions. Despite the presence of the electrostatic terms, this case is still analytically tractable, due to the dyadic form of $\tilde{q}_{ij}(k)$. Indeed, the rank of the matrices involved in such calculations turns out to be independent of the number p of components in the mixture, always being equal to the number n (typically $\ll p$) of dyads constituting the n-dyadics $\tilde{q}_{ij}(k)$. Such a feature allows to take the polydisperse $p \to \infty$ limit with an arbitrary continuous distribution of both charges and sizes.

Our findings are by no means academics. The importance of having an analytical expression of the scattering intensity for experimental purposes has been well established [45]. An application of the present results to neutron scattering experimental data will be the subject of a forthcoming paper.

A word of caution on the range of applicability of our results is in order.

The failure of the MSA closure at low densities and high charge values could be overcome by using a rescaling procedure (RMSA) [22], [23], [24]. However, this does not present a problem for many ionic fluids of current interest, which are made up of weakly charged particles at high volume fractions. In such cases the MSA is expected to be a reasonably accurate approximation, yielding semiquantitatively good predictions for the static structure factors.

Regarding the non-linear equation for the single parameter Γ, which has to be solved in the MSA scheme, selecting the physical root from the manifold of solutions is not a terribly difficult task [39]. In fact, as Hiroike [40] pointed out, this equation has only one real positive solution which is the physical one. Moreover, in their application of the MSA for charged HS to micellar solutions Senatore and Blum [27] already solved the equation for Γ even in the polydisperse limit without mentioning any particular problems.

As far as the potential considered in this work and the possibility of extending our MSA scheme to other different interactions are concerned, it is evident that the primitive model represents the simplest physically significant choice to describe ionic fluid mixtures.

The primitive model includes both attractive and repulsive Coulomb potentials and has the advantage of treating large and small ions on the same footing. For colloidal suspensions, it definitely gives a better description than the essentially one-component models which consider only the repulsive (screened) Coulomb interactions between macroions, while the other species (counter-ions, any added electrolyte and solvent) are taken into account only upon determining the screening in the effective macroion-macroion potential [38], [22], [3].

Of course, several alternative choices of potential model may be found in the literature on scattering from multicomponent fluids. For instance, very recently, Kline and Kaler [17] fitted their experimental partial structure factors of a mixed colloidal system (sodium dodecyl sulfate micelles plus Ludox colloidal silica) by a model of hard and sticky hard spheres (in the terminology of these authors, "sticky" means that an attractive square well is added outside the hard core).

Indubitably the next step after the primitive model should be the mixture of particles interacting by HS plus Yukawa ($\equiv$ screened Coulomb) potentials, i.e., $\beta\phi_{ij}(r) = K_{ij}\exp(-\mu r)/r$ for $r > \sigma_{ij}$. Unfortunately, the general MSA solution for multicomponent Yukawa fluids [41], [21] is much more involved than the MSA one for unscreened charged HS, even if substantial simplifications occur for factorizable coupling parameters, i.e., when $K_{ij} = K_i K_j$ [42], [43]. In particular, a satisfactory treatment of polydisperse Yukawa systems is still lacking. In this context, we recall that Löwen et al. [44] proposed a mapping of the polydisperse Yukawa model onto the polydisperse HS reference system. It is also worth mentioning that, to avoid the difficulty of working with the MSA solution for Yukawa mixtures, Ruiz-Estrada et al. [24] invented a method to map a Yukawa system onto an equivalent (but much easier to be treated) primitive model system. Very recently, an analytical equation of state for the HS Yukawa polydisperse fluid (in the equal-diameter case with polydispersity in the coupling parameters K_i) has been presented [46]. We believe that the Yukawa model deserves further investigation, specially on the possibility of deriving a closed MSA formula for the scattering intensity in this case as well. We are planning to do it in the near future.

Finally, before concluding this paper, we remark that our methodological recipe, based on the properties of the dyadic matrices presented in Section III, has far reaching consequences. It is indeed the property of "contraction" or "reduction" of these matrices (according to which $\left|\widehat{\mathbf{Q}}(k)\right|$ can be reduced to an equivalent determinant of very low order) that makes the evaluation of the structure factors for fluids with a large or infinite number of components a tractable problem. Our findings have also led to a simple recipe for building the inverse matrix $\widehat{\mathbf{Q}}^{-1}(k)$ for the most general $\widetilde{q}_{ij}(k)$ of dyadic form. Our formula not only includes those previously found by Blum and coworkers for $n = 2$ and $n = 3$ [13], [19], but, more

importantly, it provides a systematic way to extend the results of the present paper to new more complex cases with $n > 3$.

ACKNOWLEDGMENTS

APPENDIX A: PROOFS FOR SECTION III

I) The proof of (26) is patterned after a similar one used in the Laplace expansion of the characteristic polynomial of a $p \times p$ matrix.

Consider a $p \times p$ matrix of the generic form:

$$M_{ij} = \delta_{ij} + \widehat{W}_{ij} = \delta_{ij} + (\rho_i \rho_j)^{1/2} W_{ij} \tag{A1}$$

For the sake of simplicity, we shall work out the case $p = 3$ first and then show how the result can be generalized. Let us rewrite the determinant of the 3×3 matrix (A1) in such a way that each element is the sum of two terms (type A and type B respectively)

$$|\mathbf{M}| = \begin{vmatrix} 1 + \rho_1 W_{11} & 0 + (\rho_1 \rho_2)^{1/2} W_{12} & 0 + (\rho_1 \rho_3)^{1/2} W_{13} \\ 0 + (\rho_2 \rho_1)^{1/2} W_{21} & 1 + \rho_2 W_{22} & 0 + (\rho_2 \rho_3)^{1/2} W_{23} \\ 0 + (\rho_3 \rho_1)^{1/2} W_{31} & 0 + (\rho_3 \rho_2)^{1/2} W_{32} & 1 + \rho_3 W_{33} \end{vmatrix} \tag{A2}$$

Using elementary properties of determinants, the above expression can be written as a sum of a determinant containing only elements of type A (i.e., the identity matrix), three determinants containing two rows of type A and one of type B, three determinants containing one row of type A and two of type B and, finally, one determinant containing only rows of the type B. Hence there are 2^3 determinants overall. Again exploiting elementary properties of determinants and symmetry considerations on the permutation of the indices, one easily establishes that (A2) can be written as

$$|\mathbf{M}| = 1 + \sum_{i=1}^{3} \rho_i W_{ii} + \frac{1}{2!} \sum_{i,j=1}^{3} \begin{vmatrix} W_{ii} & W_{ij} \\ W_{ji} & W_{jj} \end{vmatrix} + \rho_1 \rho_2 \rho_3 \begin{vmatrix} W_{11} & W_{12} & W_{13} \\ W_{21} & W_{22} & W_{23} \\ W_{31} & W_{32} & W_{33} \end{vmatrix} \tag{A3}$$

The above expression can be generalized to the general p-component case, by noting that all terms with $s < p$ rows of type A and $p - s$ of type B can be written as

$$\frac{1}{(p-s-1)!} \sum_{j_1,..,j_{p-s-1}=1}^{p} \rho_1 \cdots \rho_{p-s-1} \begin{vmatrix} W_{s+1,s+1} & \cdots & W_{s+1,p} \\ \vdots & \ddots & \vdots \\ W_{p,s+1} & \cdots & W_{p,p} \end{vmatrix} \tag{A4}$$

Collecting terms of all orders yields then (26).

II) Let us now show that, if $\widehat{W}_{ij}$ is an n-dyadic (with $n < p$), then any minor of $\widehat{\mathbf{W}}$ having order $m > n$ vanishes.

We outline the proof only for $n = 2$, since its generalization to $n > 2$ is very easy. We have to show that any minor of order $m \geq 3$ is zero, but, since all minors of order $m > 3$ can be expressed in terms of the third order ones, it is sufficient to demonstrate that

$$\begin{vmatrix} \widehat{W}_{iq} & \widehat{W}_{ir} & \widehat{W}_{is} \\ \widehat{W}_{jq} & \widehat{W}_{jr} & \widehat{W}_{js} \\ \widehat{W}_{kq} & \widehat{W}_{kr} & \widehat{W}_{ks} \end{vmatrix} = 0 \qquad \forall (i,j,k,q,r,s) \tag{A5}$$

If $\widehat{W}_{ij} = a_i^{(1)} b_j^{(1)} + a_i^{(2)} b_j^{(2)}$ and if we define

22

$$\lambda_i \equiv a_i^{(2)}/a_i^{(1)} \qquad \text{and} \qquad \mu_j \equiv b_j^{(2)}/b_j^{(1)} \qquad (\text{if} \quad a_i^{(1)} \neq 0, \ b_j^{(1)} \neq 0), \qquad (A6)$$

then we could write $\widehat{W}_{ij} = a_i^{(1)} b_j^{(1)} (1 + \lambda_i \mu_j)$. Substituting this expression into the determinant of eq. (A5) and factoring out all common factors, we get

$$a_i^{(1)} a_j^{(1)} a_k^{(1)} b_i^{(1)} b_j^{(1)} b_k^{(1)} \begin{vmatrix} 1 + \lambda_i \mu_q & 1 + \lambda_i \mu_r & 1 + \lambda_i \mu_s \\ 1 + \lambda_j \mu_q & 1 + \lambda_j \mu_r & 1 + \lambda_j \mu_s \\ 1 + \lambda_k \mu_q & 1 + \lambda_k \mu_r & 1 + \lambda_k \mu_s \end{vmatrix} \qquad (A7)$$

Then, by subtracting the third row from both the first and the second one, we see that the resulting determinant vanishes since two rows are proportional.

III) As concerns $|\mathbf{M}|$ expressed in terms of $\delta_{\mu\nu} + \mathbf{a}^{(\mu)} \cdot \mathbf{b}^{(\nu)}$, eq. (28) can be verified very rapidly for $n = 2$, by using eq.s (26) and (A5) together with the following identity

$$\begin{vmatrix} \widehat{W}_{iq} & \widehat{W}_{ir} \\ \widehat{W}_{jq} & \widehat{W}_{jr} \end{vmatrix} = \left[a_i^{(1)} a_j^{(2)} - a_i^{(2)} a_j^{(1)} \right] \left[b_q^{(1)} b_r^{(2)} - b_q^{(2)} b_r^{(1)} \right], \qquad (A8)$$

which holds true for 2-dyadics.

IV) Finally, in order to prove eq.s (30)-(32) for the cofactors, one first establishes that the elements M_{ij}^{-1} of the inverse matrix can be computed order by order in the ρ's, by using the definition

$$\sum_{k=1}^{p} M_{ik}^{-1} M_{kj} = \delta_{ij} \qquad (A9)$$

This leads to the following result

$$M_{ij}^{-1} = \delta_{ij} - (\rho_i \rho_j)^{1/2} W_{ij} + (\rho_i \rho_j)^{1/2} \sum_{k=1}^{p} \rho_k W_{ik} W_{kj} - (\rho_i \rho_j)^{1/2} \sum_{k,l=1}^{p} \rho_k \rho_l W_{ik} W_{kl} W_{lj} + \dots$$
$$(A10)$$

Then, starting from $|\mathbf{M}|^{\mathbf{ji}} = \mathbf{M}_{\mathbf{ij}}^{-1} |\mathbf{M}|$, using the expansion (26) for $|\mathbf{M}|$ and collecting all terms of the same order, one finds, after some simple algebra, the required expansion.

APPENDIX B: COMPARISON BETWEEN DIFFERENT NOTATIONS

In place of Baxter's factorization expressed by eq. (13), Blum and coworkers [13], [18], [19], [41] start from

$$\mathbf{I} - \mathbf{C(k)} = \widehat{\mathbf{Q}}(\mathbf{k}) \widehat{\mathbf{Q}}^{\mathbf{T}}(-\mathbf{k}) \qquad (B1)$$

where the elements of $\widehat{\mathbf{Q}}(k)$ are again of the form

$$\widehat{\mathbf{Q}}(k) = \mathbf{I} - \widetilde{\mathbf{Q}}(k), \qquad (B2)$$

but with

$$\widetilde{\mathbf{Q}}(k) = 2\pi \int_{-\infty}^{+\infty} dr \ e^{ikr} \mathbf{Q}(\mathbf{r}) \qquad \text{and} \qquad \mathbf{Q_{ij}(r)} = (\rho_i \rho_j)^{1/2} \mathbf{q_{ij}(r)} \qquad \text{(B3)}$$

This choice leads to a slightly different version of the equations for the factor correlation functions, namely to

$$
\begin{cases}
2\pi r c_{ij}(|r|) = -q'_{ij}(r) + \sum_m \rho_m \int_{\lambda_{mj}}^{\infty} dt \ q_{jm}(t) \, q'_{im}(r+t), & r > \lambda_{ji} \equiv \tfrac{1}{2}(\sigma_j - \sigma_i) \\[2mm]
2\pi r h_{ij}(|r|) = -q'_{ij}(r) + 2\pi \sum_m \rho_m \int_{\lambda_{jm}}^{\infty} dt \ (r-t) \, h_{im}(|r-t|) \, q_{mj}(t), & r > \lambda_{ji}
\end{cases}
\qquad \text{(B4)}
$$

The correspondence between our (or Baxter's) notation and Blum's one is very simple

$$q_{ij}^{Baxter}(r) = \frac{1}{2\pi} q_{ji}^{Blum}(r) \qquad \text{(B5)}$$

As a consequence, our q'_{ij}, q_i'' and A_i are easily obtained from Blum's counterparts by performing index transposition and division by 2π.

Finally, our P_z and Ω correspond, respectively, to $\Delta^{-1} P_N$ (or $\Delta^{-1} P_n$) and $\Omega\Delta$ of Blum's papers.

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